Direct Correlation of Transition Metal Impurities and Minority Carrier Recombination in Multicrystalline Silicon

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Impurity and minority carrier lifetime distributions were studied in as-grown multicrystalline silicon used for terrestrial-based solar cells. Synchrotron-based x-ray fluorescence and the Light Beam Induced Current technique were used to measure impurity and lifetime distributions, respectively. The purpose of this work was to determine the spatial relation between transition metal impurities and minority carrier recombination in multicrystalline silicon solar cells. Our results reveal a direct correlation between agglomerations of chromium, iron and nickel impurities with regions of high minority carrier recombination. These results provide the first direct evidence that transition metal agglomerates play a significant role in solar cell performance.

Multicrystalline silicon can be used to fabricate solar cells with moderate solar conversion efficiency and low fabrication costs. These cells are presently manufactured for terrestrial-based applications; however, an improvement in the efficiency of these cells would greatly increase their commercial viability, see [1-3]. The primary cause for lowered efficiencies is localized regions of high minority carrier recombination. These regions possess high concentrations of dislocations [4-6]. It is known that minority carrier recombination at dislocations themselves is relatively weak but greatly increases by decoration or precipitation of transition metal impurities [7-10]. This suggests that dislocations in high recombination regions of mc-silicon are decorated with transition metals, however, past research has not presented direct evidence showing the source for carrier recombination at these dislocations. Past work has revealed that metal impurity agglomerations are present at dislocations in mc-silicon [11], however, no correlation was established to carrier recombination. This research seeks to determine whether a correlation between metal impurity distributions and regions of high minority carrier recombination exists in mc-silicon solar cells.

The polycrystalline wafers were formed by an electromagnetic casting method [12], followed by sawing and chemical etching to remove saw damage. Minority carrier recombination was mapped across the as-grown material with the light beam induced current (LBIC) method. The frontside of the samples were analyzed using synchrotron-based XRF mapping in order to determine metal impurity content and distribution. The XRF equipment is located at the Center for X-ray Optics microprobe beamline in the Advanced Light Source Center. It uses 12.5keV monochromatic radiation to excite elements in the sample with a spatial resolution of $1\mu m^2$ and a Si-Li detector to measure fluorescence x-rays from the sample, all in atmospheric conditions. Etch features on the sample surface, caused by slight preferential etching of grain boundaries during the silicon etch prior to Al contact formation, were used as reference points to locate regions of interest.

LBIC mapping of minority carrier recombination across the mc-silicon sample revealed localized regions of high carrier recombination. A typical LBIC map in a portion of the material is shown in Figure 1 where dark regions indicate areas of high carrier recombination. Of particular interest is the band of high carrier recombination located approximately in the center of the scan area.

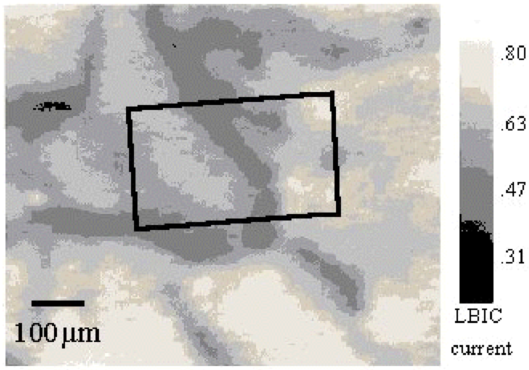

Figure 1. Light Beam Induced Current of carrier recombination across multicrystalline silicon. Dark regions indicate high carrier recombination. The black box denotes the area analyzed with x-ray fluorescence.

X-ray Fluorescence (XRF) spectra were taken at $1\mu m^2$ points in the region of Figure 1 as denoted by the black box. Typical spectra are shown in Figure 2. No x-ray fluorescent radiation associated with impurities was measured in regions of the mc-silicon with low minority carrier recombination. However, x-ray fluorescent radiation associated with the 3d transition metals was found in regions of the material with high carrier recombination. As seen in Figure 2, the Fe Kα and Fe Kβ fluorescence radiation are clearly discernable above background noise. The ratio of these spectral peak heights is approximately 4:1 for Kα to Kβ. This ratio is in accordance with the expected intensity ratio of Kα to Kβ radiation defined by the electron transition probability. The presence of both Fe Kα and Fe Kβ radiation, with the expected intensity ratios, acts as fingerprint for the presence of Fe and provides direct evidence that Fe is present in this region of the material. Fluorescent radiation at 5.4 keV and 7.47 keV is also clearly distinguished above background noise while small spectral peaks at 5.95 keV and 8.26 keV are only slightly above background. The intense peaks at 5.4 and 7.47 keV concur with the energies of Cr Kα and Ni Kα fluorescent radiation, respectively, while the presence of weaker peaks at 5.95 and 8.26 keV correspond with Cr Kβ and Ni Kβ fluorescent radiation, respectively. Considering the expected intensity ratio of Kα to Kβ for both Cr and Ni is 4:1, and the peak intensity of the presumed Cr Kα and Ni Kα spectral peaks at 5.4 keV and 7.47 keV is only 10 counts, the expected peak intensity of Cr Kβ and Ni Kβ coincides with the approximate intensity of the weaker peaks. This provides strong evidence that Cr and Ni impurities are present in this region of the material.

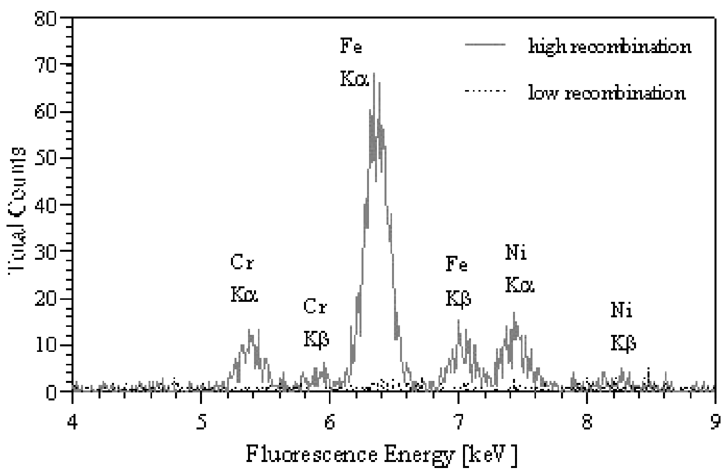

Figure 2. X-ray fluorescence spectra taken in high and low minority carrier recombination regions of multicrystalline silicon. Data was taken at points in the region denoted by the black box of Figure 1. Note the fluorescent signal of Cr, Fe, and Ni in the high-recombination region.

Concentrations of impurities at each $1\mu m^2$ spot were calculated by analysis of the collected spectra in comparison to standard samples with known concentrations of impurities. Impurity maps were produced in the region denoted by the black box in Figure 1. Figures 3a,b and c are impurity maps of Cr, Fe and Ni in this region. Clearly there is a correlation between metal impurity distributions and minority carrier recombination. This is the first direct proof that metal impurity agglomerates play a significant role in mc-silicon solar cell performance.

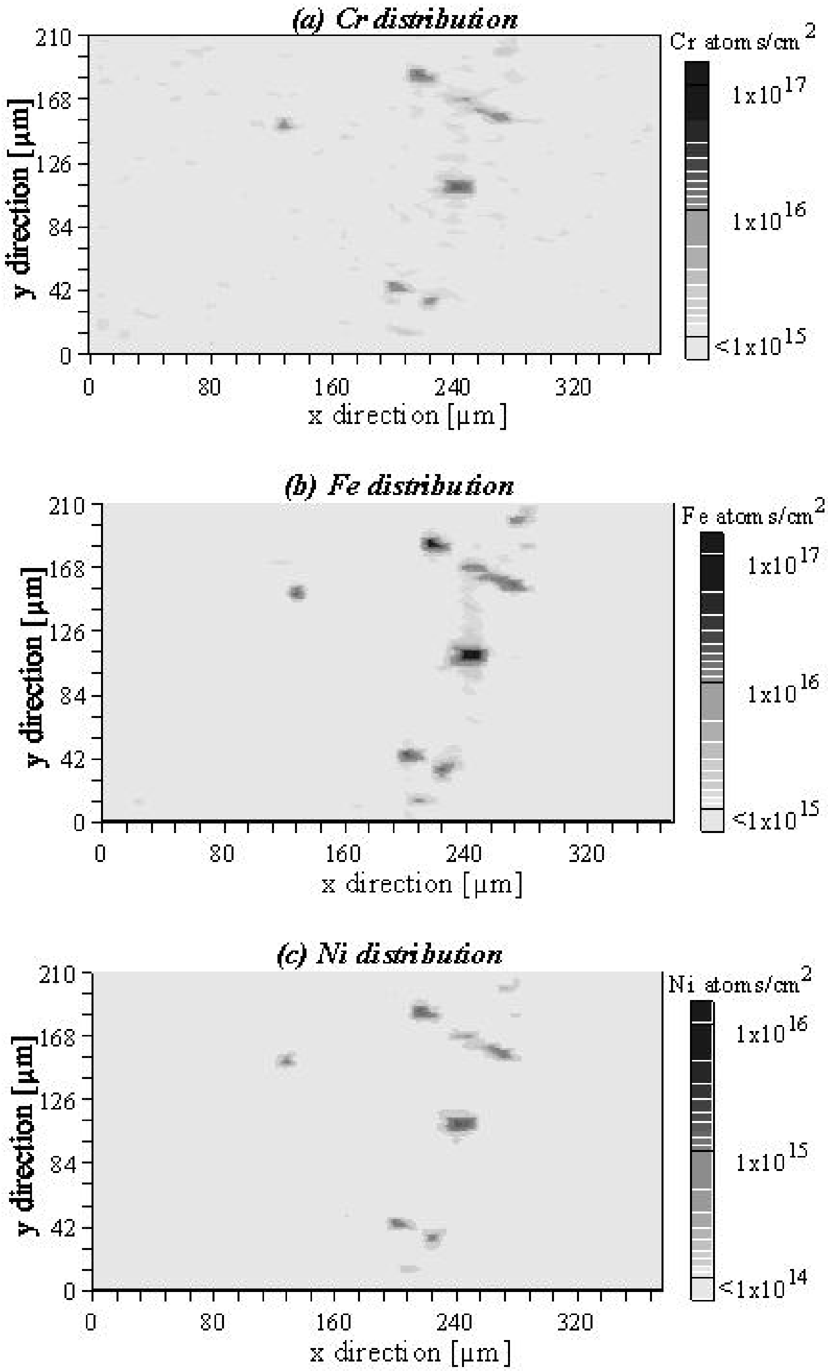

Figure 3. a) Cr, b) Fe and c) Ni distributions in multicrystalline silicon. The mapped area directly corresponds to the area in the black box of Figure 1. Note the correlation between metal impurity distributions and carrier recombination.

In conclusion, Cr, Fe and Ni metal impurities were found in electromagnetically cast multicrystalline silicon used for solar cells. The distribution of impurities correlated directly with regions of high minority carrier recombination. The work presented here is the first direct proof that metal impurity agglomerates significantly affect the performance of multicrystalline silicon solar cells.

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